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Surface-confined [2+2] Cycloaddition Towards One-dimensional Polymers Featuring Cyclobutadiene Units

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Surface-confined synthesis has been offering a wide range of opportunities for the construction of novel molecular nanostructures. Exploring new types of on-surface coupling reactions is considered essential for being able to deliberately tune the materials properties. Here, we report on the formation of a covalent C–C bonding motif, namely 1,3-cyclobutadiene, via surface-confined [2+2] cycloaddition between pyrene moieties using low temperature scanning tunneling microscopy (LT-STM) and X-ray photoemission spectroscopy (XPS) measurements. By employing a hydrogen dosing treatment together with low-temperature activation, we were able to both eliminate residual byproducts and obtain covalent 1D polymers through the formation of 1,3-cyclobutadiene units. The results present a C–C bonding motif hardly explored in surface chemistry and provide substantial evidence that the hydrogen treatment is crucial towards the removal of byproducts in surface-confined polymerization.

Introduction

Around one decade ago, surface-confined synthesis under ultra-high vacuum (UHV) conditions was introduced as an alternative method to traditional solution-based synthesis for the bottom-up fabrication of low dimensional π -conjugated nanostructures.^{1–8} This method has opened up new possibilities for the construction of extended molecular nanoarchitectures on surfaces in a controlled fashion, offering a versatile playground for potential applications in future electronic devices.^{8–12} In this context, different types of chemical reactions have been employed for the fabrication of tailored 1D and 2D covalent nanostructures, including Ullmann-type coupling,^{1,10,13–19} cyclodehydrogenation,¹⁰ condensation reactions,²⁰ acetylenic homocouplings (i.e., Glaser or Hay coupling),^{21,22} alkane dehydrogenation²³ and others.^{3,24–26} To date, Ullmann-type coupling has been the most frequently used reaction. However, the halogen atoms split off during the polymerization reaction have been often observed to chemisorb on the metal surface and thus, are an undesired reaction byproduct, which can in turn cause

structural modifications of the surface,^{27–30} and may even hamper the diffusion of the monomers which is important during the polymerization process. Therefore, it negatively influences the formation of well-ordered polymer structures. To desorb the split off halogen atoms from the metal surface, one generally needs to anneal the sample at high temperatures (> 523 K).^{31–33} However, such high temperatures may negatively influence the formed polymer networks or even destroy them. Recently, an alternative approach based on hydrogen dosing during the activation of the on-surface reaction and verified by temperature-programmed desorption measurements was presented for desorbing the split off halogen atoms during the polymerization reaction.³⁴ However, hitherto there has been no direct microscopic visualization of the outcome of this process.

The formation of covalent C–C bonds of a 4-membered 1,3-cyclobutadiene ring, involving two endocyclic C=C bonds through a [2+2] cycloaddition of intermediate arynes (or biradicals), has been already known in solution.^{35–38} However, reports for such an interesting covalent dimerization are scarce under UHV conditions. A recent related work focused on the surface-confined formation of phthalocyanine derivatives on Au(111), where the 4-membered ring was formed by dimerization of alkenes and hence, it does not possess any endocyclic C=C bonds.³⁹ Another interesting study employed a perylenetetracarboxylic dianhydride derivative to synthesize graphene-type nanoribbons involving 4- and 8-membered rings which were formed via a stepwise process.⁴⁰ Hence, up to now no direct experimental evidence of such a dimerization involving aryne intermediates in surface chemistry has been reported.

In this work, we also present a new on-surface synthesis protocol under UHV conditions for the formation of 1,3-butadiene units connecting pyrene derivatives into a 1D

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covalent polymer. Using 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (**1**) as a molecular precursor, we investigated both the self-assembly and on-surface polymerization on coinage metal surfaces by STM and XPS measurements. We obtained well-ordered 2D self-assembled networks for the deposition of **1** on Au(111) held at room temperature. Upon thermal activation above 450 K combined with hydrogen dosing, the network undergoes covalent polymerization through the formation of 4-membered rings between the pyrene units. However, for the more active Cu(111) surface, we directly obtained 1D metal-coordinated polymer chains by deposition of **1** on the substrate held at room temperature.

Results and discussion

Deposition of submonolayer coverage of **1** on Au(111) held at room temperature results in self-assembled structures in two different arrangements with a relatively equal distribution: phases A and B. Fig. 1a and 1c present detailed STM images of phases A and B, respectively (for an overview STM image see Fig. S1). The characteristic Au(111) herringbone reconstruction is visible through the molecular adlayer and remains unaffected, which we ascribe to a weak molecule-substrate interaction.⁴¹ In the close-up STM image (Fig. 1a), the molecular structure of **1** is superimposed. The bright protrusions are ascribed to the *tert*-butyl groups.^{42,43} Fig. 1b shows the tentative model revealing the intermolecular interactions for the observed 2D pattern. The molecules are arranged in a rhombic unit cell with parameters $a_1 = 1.30 \pm 0.12$ nm, $a_2 = 1.60 \pm 0.14$ nm and $\alpha = 44 \pm 2^\circ$. The direction a_2 draws an angle of about 80° with the Au [110] direction. Taking into account the possible non-covalent interactions,^{41,44–46} we conclude that both weak intermolecular hydrogen bonds (along d_1) and van der Waals forces (along d_2) are responsible for the well-ordered phase A. Here, the average interaction distances are $d_1 = 3.7 \pm 0.1$ Å (between Br and H in the *tert*-butyl groups of the neighboring molecules, marked by the red dotted lines) and $d_2 = 2.7 \pm 0.1$ Å (between H and H in the neighboring *tert*-butyl groups, marked by the black dotted lines), which are in good agreement with literature.^{41,44–46} Note that in our interpretation the halogen bonds between Br-Br of two neighboring molecules are neglected since the Br-Br distance $d_{\text{Br-Br}}$ is too large (> 4.5 Å).

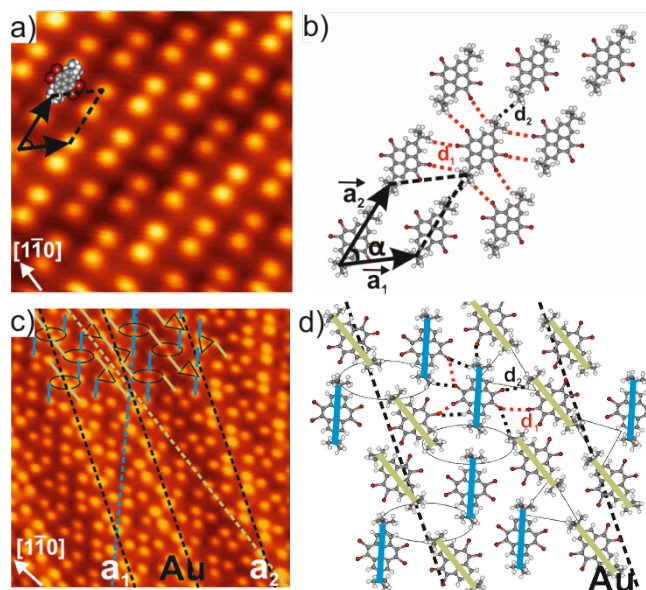


Fig. 1. 2D self-assembled structure of **1** on Au(111). a) (5×5 nm²; 20 pA, -1.5 V) Topographic STM image of phase A showing a well-ordered self-assembled network with a molecule **1** and the rhombic unit cell superimposed. b) Tentative model for phase A. c) (10×10 nm²; 20 pA, -1.5 V) STM image of phase B. The superimposed blue and light green short lines illustrate molecules **1** aligned parallel to either the a_1 (blue dotted line) or a_2 (light green dotted line) directions. The triangles and ellipses indicate the groups of three and four joint molecules, respectively. The black dotted lines indicate the Au [112] direction. d) Tentative model for phase B.

Fig. 1c shows a detailed STM image of phase B, which is, however, a rather complex molecular arrangement compared to phase A. From overview STM images (Fig. S2), one can observe a long-range periodicity of the groups of either three or four bright protrusions with the herringbone reconstruction easily visible underneath the molecular layer. These groups of three and four protrusions are labeled by triangles and ellipses in Fig. 1c. The molecules tend to align along the directions labeled a_1 or a_2 , which draw an angle of $\sim 22^\circ$ with the Au [112] direction. The obtained phase B is stabilized by a combination of both hydrogen and halogen bonding.^{45,46} Here, the measured distances d_1 (between Br and Br of the neighboring molecules) and d_2 (between Br and H of the nearby molecules) amount to 3.3–3.9 Å and 2.1–3.6 Å, respectively. It should be noted that for this phase the repulsive interaction, due to the C–Br...Br–C angle (type-I interactions), between the halogens plays a role in forming the self-assembled network.^{41,46}

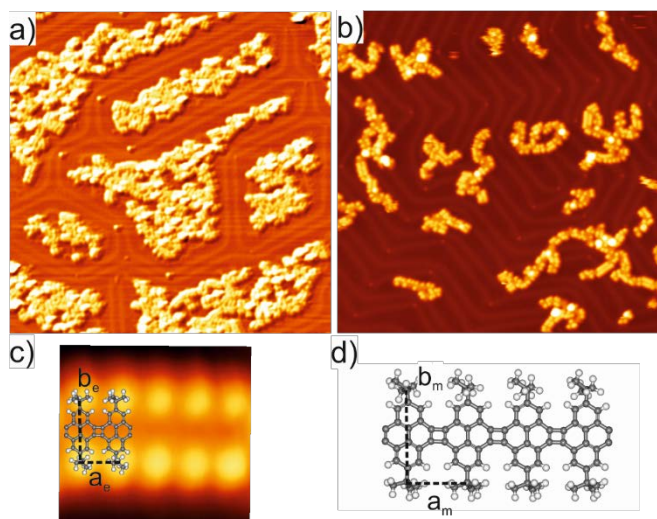


Fig. 2. On-surface polymerization of **1** on Au(111). a) (70 x 70 nm²; 20 pA, -1.5 V) STM image showing islands of disordered polymer after annealing the sample at 550 K. b) (50 x 50 nm²; 20 pA, -1.5 V) STM image showing 1D polymer chains after dosing hydrogen for 2h while keeping the substrate at 450 K. c) (2.8 x 2.8 nm²; 30 pA, -1.5 V) Detailed STM image showing a part of a 1D polymer chain. Two monomers are superimposed. d) Tentative model for the observed 1D polymer chains.

Fig. 2 illustrates the on-surface polymerization of **1** on Au(111) upon thermal activation. The submonolayer coverage sample was annealed at 550 K for 20 minutes and subsequently cooled to 77 K for the STM measurements. However, we could not observe any well-ordered polymer patterns. Instead, disordered islands were observed and the herringbone reconstruction was affected as shown in Fig. 2a. At this annealing temperature, the dissociation of C–Br bonds occurs. The split off Br atoms do not desorb but stay adsorbed on the Au surface.³⁰ The presence of the pronouncedly electronegative halogen atoms may give rise to the release of Au atoms from the surface, leading to the modification of the reconstructed surface.^{27–30} We could not observe any ordered polymeric networks even when annealing the sample at higher temperatures (beyond 600 K). The reason for observing these disordered polymer islands is assigned to the existence of a large amount of the split off Br atoms, which might in turn strongly influence the diffusion of the activated monomers and thus, their covalent linking. Similarly, in our recent study on 1,3,6,8-tetrabromopyrene on Au(111), additional sample annealing up to very high temperatures (723 K) did not help to improve the quality of the polymeric network.³⁰

In order to eliminate the split off Br from the substrate, we employed a hydrogen dosing treatment. By this approach, the Br atoms released during the C–Br bond scissions are able to desorb from the surface in the form of HBr.³⁴ After optimizing the treatment parameters, i.e., annealing temperature, H₂ dosing pressure and time, a total dosage of 720 Langmuir of H₂ at a partial pressure of $p_{\text{H}_2} = 2 \times 10^{-7}$ mbar during $t = 2$ hours was used, while keeping the substrate at 450 K. Now, individual 1D polymer chains could be observed while the Au herringbone reconstruction stayed intact (Fig. 2b). That corroborates the absence of adsorbed split off Br atoms on the substrate. Fig. 2c presents a high resolution STM image of a 1D chain. In this case, two endocyclic C=C bonds stabilize

the formation of the chains as shown in a tentative model in Fig. 2d. The length distribution of the 1D polymers is presented in Fig. S4. The average distances between two nearest bright protrusions along and perpendicular to the chain amount to $a_e = 0.56 \pm 0.03$ nm and $b_e = 1.00 \pm 0.05$ nm, respectively (Fig. 2c). The experimental lengths are in excellent agreement with the distances determined from the proposed model structure for the bonding mechanism of the polymer chains, where $a_m = 0.58$ nm and $b_m = 1.03$ nm (Fig. 2d). In essence, the formation of the covalent polymer involving the 4-membered rings between the pyrene units is intriguing. The formation of such 1,3-cyclobutadienes via the [2+2] cycloaddition of intermediate arynes (or biradicals), has been well known in solution.^{35–38} Hence, our results provide clear evidence on the formation of covalent 1,3-cyclobutadiene-fused pyrene polymers under UHV conditions on a surface.

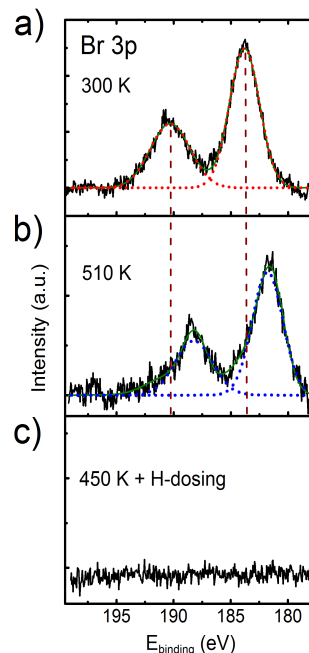


Fig. 3. XPS measurements for **1** on Au(111). a) Br 3p XPS spectrum for the core-level of the self-assembled network of **1** showing two pronounced peaks at 183.9 eV and 190.4 eV. The molecular deposition was performed at room temperature. b) Br 3p XPS spectrum for annealing the sample at 510 K. Two new components appear at lower binding energies (i.e., 181.8 eV and 188.2 eV), which can be associated with split off Br atoms residing on the Au surface. c) XPS spectrum after dosing hydrogen for 2 hours while keeping the substrate at 450 K obviously shows the absence of split off Br atoms on the surface.

To gain further insight into the surface-assisted polymerization, we studied **1** on Au(111) by means of X-ray photoemission spectroscopy (XPS; Fig. 3). Fig. 3a shows the Br 3p XPS spectrum of the self-assembled network for the molecular deposition performed at room temperature. The spectrum was fitted with a single doublet showing two peaks located at 190.4 eV and 183.9 eV which correspond to the Br 3p_{1/2} and 3p_{3/2} component, respectively. The peak positions are indicative for intact Br–C bonds which is in good agreement with previous studies.^{47,48} The spectrum obtained for the sample annealed at 510 K was fitted with a single doublet, showing the Br 3p_{1/2} and 3p_{3/2} components situated at 188.2 eV and 181.8 eV (Fig. 3b). This is an indication for split off Br atoms due to annealing.⁴⁷ Therefore, these results clearly show that Br atoms were split off during the annealing step but they did not desorb from the Au surface. Note that even for annealing temperatures up to 573 K, the split off Br atoms were found to be present on the Au(111) surface.³⁰ Fig. 3c shows an XPS spectrum of the sample annealed together with the hydrogen treatment using the same procedure as for the STM measurements (Fig. 2b). In this case, within the same binding energy window we do not observe any sign of chemisorbed Br atoms on the Au(111) surface. Note that density functional theory and temperature-programmed desorption studies were recently

carried out to demonstrate the removal of Br atoms by the H-treatment.³⁴ Thus, we conclude that with the help of thermal activation and hydrogen treatment, we are able to obtain covalent 1D 1,3-cyclobutadiene-fused pyrene polymers accompanied by a complete removal of halogen byproducts, which is corroborated by the excellent agreement between STM and XPS data.

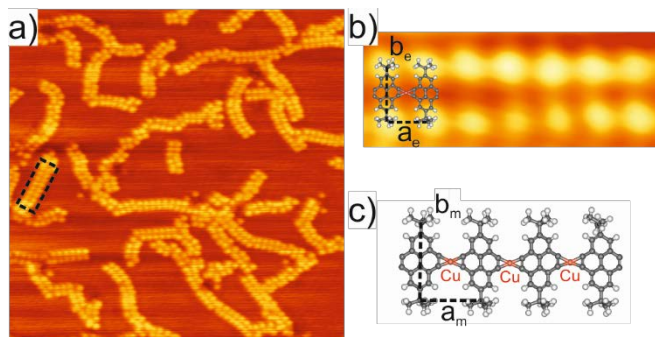


Fig. 4. Deposition of **1** on Cu(111) held at room temperature. a) (50 x 50 nm²; 30 pA, -1.6 V) STM image visualizing 1D coordination polymer chains. b) (6.5 x 2.5 nm²; 30 pA, -1.8 V) Close-up STM image of a 1D polymer chain (the black dotted rectangle in a)). Two monomers are superimposed. c) Tentative model proposed for the 1D polymer chains.

To shed further light on the formation of the polymeric network of **1** on metal surfaces, we used Cu(111) which has a higher catalytic activity than Au(111).⁴⁹ Compound **1** was deposited on a clean Cu(111) surface held at room temperature and subsequently cooled to 77 K for the STM measurements. As shown in Fig. 4a, 1D polymer chains were clearly formed, which implies that the debromination already occurs at room temperature. This finding is well in line with previous studies.^{30,50–52} The scission of the C–Br bonds on Cu(111) is further confirmed by XPS data, showing two pronounced peaks corresponding to the Br 3p binding energies of dissociated Br atoms chemisorbed on the surface (Fig. S5). From close-up STM images like the one in Fig. 4b, we determined the average distances to be $a_e = 0.80 \pm 0.05$ nm and $b_e = 1.00 \pm 0.06$ nm. It should be noted that the distance a_e between two nearest molecules in the chain is 0.24 nm larger than the one measured in the case of the covalently linked polymer chains on Au(111). This suggests the formation of 1D coordination polymers on Cu(111). The length distribution of the 1D metal-coordinated polymers is presented in Fig. S6. The proposed model (Fig. 4c) exhibits distances $a_m = 0.78$ nm and $b_m = 1.03$ nm which fit with the experimentally determined ones. Furthermore, the proposed model as well as the bonding distances for the C–Cu–C metal-ligand bonds (Cu–C distance of 1.6 Å) are in agreement with literature.⁵² Note that we could not observe any covalently linked polymers upon annealing the sample to 573 K on Cu(111).

Conclusions

In conclusion, we investigated the self-assembly and on-surface polymerization of 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene on Au(111) and Cu(111) surfaces under UHV conditions. On the Au substrate two self-assembled phases stabilized by weak hydrogen bonds, van der Waals interactions

and halogen bonds were observed. By employing thermal activation with concurrent hydrogen treatment we achieved a ‘clean’ on-surface polymerization through the [2+2] cycloaddition of the intermediary formed arynes (or biradicals). In contrast, on the Cu(111) substrate with higher catalytic activity, the observed 1D polymeric chains are stabilized by metal-coordinated bridges. Importantly, our findings present a 4-membered 1,3-cyclobutadiene ring via the surface-confined [2+2] cycloaddition which has not been reported so far. Moreover, the employed H-dosing treatment was shown to desorb the unwanted and hindering polymerization byproducts (Br in our case) thereby facilitating the formation of the 1D polymers as well as superior structural quality. Thus, the H-dosing treatment is regarded as a promising method for fabricating covalently linked nanostructures at reduced activation temperatures with improved structural ordering via Ullmann-type coupling.

Conflicts of interest

There are no conflicts to declare.

Experimental methods

4,5,9,10-Tetrabromo-2,7-di-*tert*-butylpyrene (**1**) was synthesized according to the literature procedure.⁵³ All STM experiments were performed in a two-chamber UHV system (Oxford Instruments Omicron NanoScience) with a base pressure of 2×10^{-11} mbar at liquid nitrogen temperature (77 K). The Au(111) and Cu(111) single crystals were cleaned by subsequent cycles of sputtering with Ar⁺ ions and annealing at 500° C and 480° C, respectively. The molecules were thermally evaporated from a glass crucible that was heated inside a home-built evaporator. A quartz-crystal microbalance was used to monitor the molecular deposition rate while the metal substrates were held at room temperature during deposition. All STM images were taken in constant current mode using a platinum-iridium tip. Image processing was done with the free software WSxM.⁵⁴

The XPS measurements were performed in another two-chamber UHV system using a hemispherical energy analyser employing Al K α radiation with a photon energy of 1468.6 eV. The sample preparation was carried out in the same way as mentioned for the STM measurements. The Au 4f core level spectra were taken for referencing the XPS data.

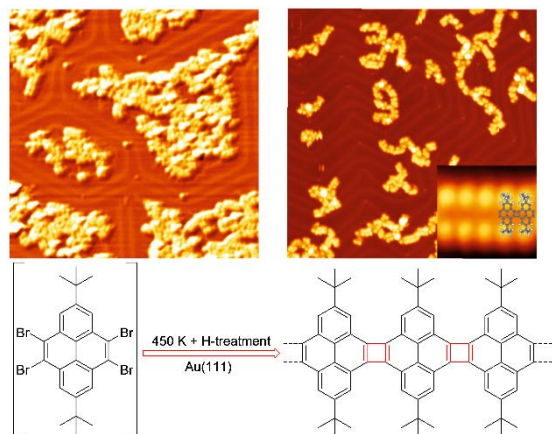
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We report on the formation of 1,3-butadiene units between pyrene moieties through surface-confined [2+2] cycloaddition polymerization under ultrahigh vacuum conditions. We successfully demonstrated that the employed H-dosing treatment is a promising method for fabricating covalently linked nanostructures at reduced activation temperatures with improved structural ordering.